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Aug 27, 1999

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TITLE: PHOTOVOLTAIC DEVICE AND ITS MANUFACTURE

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APPL-NO: JP10034660

APPL-DATE: February 17, 1998

INT-CL (IPC): H01 L 31/04; H01 L 21/205

## ABSTRACT:

PROBLEM TO BE SOLVED: To improve a short-circuiting light current and an open terminal voltage, at the same time reduce light deterioration, improve the conversion efficiency of a photovoltaic device, and improve productivity, by changing the crystallization rate and the hydrogen content of a non-monocrystalline silicon in an i-type semiconductor layer in the direction of a layer thickness.

SOLUTION: A photovoltaic device has a semiconductor layer in a pin structure where a p-type semiconductor layer 103, an i-type semiconductor layer 104, and an n-type semiconductor layer 105 are laminated, and the i-type semiconductor layer 104 is made of a non-monocrystalline silicon. In this case, the crystallization rate and the hydrogen content of the non-crystalline silicon in the i-type semiconductor layer 104 are changed in the direction of a layer thickness. In that case, a fine crystal silicon is preferable as the non-monocrystalline silicon, and the i-type semiconductor layer 104 preferably contains Ge or C and, specifically,

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TITLE: Photovoltaic cell for solar batteries - comprises pin-type semiconductor layer, in which i-type semiconductor layer is of amorphous silicon

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ABSTRACTED-PUB-NO: JP 11233803A

BASIC-ABSTRACT:

NOVELTY - The semiconductor layer of the photovoltaic cell comprises a p-type semiconductor layer, an i-type semiconductor layer and an n-type semiconductor layer. The i-type semiconductor layer comprises amorphous silicon whose rate of crystallization and hydrogen content change in the thickness direction.

DETAILED DESCRIPTION - An INDEPENDENT CLAIM is also included for the production of the photovoltaic cell.

USE - For solar batteries.

ADVANTAGE - The conversion efficiency, curvilinear factor and short circuit current density of the photovoltaic cell are improved.

DESCRIPTION OF DRAWING(S) - The figure shows a schematic model sectional view of the photovoltaic cell.

CHOSEN-DRAWING: Dwg.1/4

TITLE-TERMS: PHOTOVOLTAIC CELL SOLAR BATTERY COMPRISE PIN TYPE SEMICONDUCTOR LAYER TYPE SEMICONDUCTOR LAYER AMORPHOUS SILICON

DERWENT-CLASS: L03 U11 U12

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DETAILED DESCRIPTION

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## [Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates mainly to the reliability of a photovoltaic cell and the improvement in a conversion efficiency using microcrystal silicon in more detail about pin [ which has non-single crystal silicon, such as amorphous silicon and microcrystal silicon and polycrystal silicon, ] type photovoltaic cells and those manufacture methods.

[0002]

[Description of the Prior Art] In recent years, carbon-dioxide-emissions curtailment is cried for as a cure of global warming prevention. Then, the photovoltaics which do not discharge a carbon dioxide attract attention. Conventionally, the system which used the single crystal and the polycrystal has been used for the solar battery. Especially, in single crystal silicon, that to which a conversion efficiency exceeds 20% has also appeared. However, shortage of the silicon wafer used as a raw material has been a problem as a solar battery spreads through a commercial scene. It is because supply of a raw material has stopped catching up with the standup of the commercial scene of a solar battery although the remainder of the silicon wafer for IC has been used for the solar-battery material of a single crystal and a polycrystal. Then, the solar battery using amorphous silicon as a system which does not use a crystal has been proposed. As the deposition method of the hydrogenation amorphous silicon used for these semiconductor devices, or microcrystal silicon, RF plasma CVD method which makes a silane SiH<sub>4</sub> or disilane Si<sub>2</sub>H<sub>6</sub> membrane formation gas, the microwave plasma CVD method, or the reactive-sputtering method which carries out the spatter of the Si target in Ar plasma under hydrogen gas existence has been used.

Experimentally, in addition to this, there are optical CVD, the ECRCV method, a vacuum deposition method of Si under hydrogen atom existence, etc. The plasma CVD method has spread most by the method of producing such hydrogenation amorphous silicon and microcrystal silicon. With this method, using a silane SiH<sub>4</sub> and disilane Si<sub>2</sub>H<sub>6</sub>, it dilutes with hydrogen gas if needed, plasma is generated in a 13.56MHz RF, the active species which decomposes membrane formation gas by plasma and has reactivity is built, and a film is made to deposit on a substrate by it. Moreover, if doping gas, such as a phosphine (PH<sub>3</sub>), a diboron hexahydride (B<sub>2</sub>H<sub>6</sub>), and BF<sub>3</sub>, is mixed with membrane formation gas, a n-type semiconductor and a p type semiconductor can be formed.

[0003] By the way, with hydrogenation amorphous silicon, it had to be ready for the fall of the property by photodegradation, and the solar-battery device of the high conversion efficiency in a low cost was not able to be formed. Moreover, in the case of an amorphous-silicon solar cell, a conversion efficiency will become bad if light is irradiated. If light is irradiated, the silicon dangling bond used as the recombination center of the generated optical carrier will increase. Therefore, if it leaves for a long time on the bottom of sunlight, the conversion efficiency of a solar battery will fall. The attempt with how to use microcrystal silicon for a solar battery in recent years is made under such a background.

[0004]

[Problem(s) to be Solved by the Invention] Although the cause that a silicon dangling bond is formed in the case of an amorphous-silicon solar cell is not clear, in order to carry out power application of the amorphous-silicon solar cell, to form a solar battery without photodegradation is desired. Then, development of the microcrystal silicon characterized by the microcrystal phase in which the part in perfect silicon that it is not amorphous and amorphous forms a crystal phase is performed. Although promising \*\* is carried out in the microcrystal since it excels in light stability compared with amorphous silicon, there are many defects in the conventional state. Moreover, since a band gap has only a crystal silicon grade, compared with the case where open end voltage is amorphous silicon, it is small, and it is difficult to obtain the big thing of a conversion efficiency. For example, the group of the Neuchatel university in Switzerland succeeded in raising a conversion efficiency to 4.6% by the VHF plasma CVD method. However, open end voltage is obtained only about 0.39V. Although open end voltage improved to about 0.60-0.78V by application of p layers of amorphous silicon carbide, and introduction of an p/i volume phase, the curvilinear factor fell greatly, and the conversion efficiency was the result of falling after all. With microcrystal silicon, a band gap is about 1.1eV, and it is smaller than band-gap about 1.7eV of an amorphous silicon. Therefore, in the solar battery, muc-Si is expected as the bottom of the stack type cell produced combining i layers more than a bilayer, or a cell for middle. The carrier generated when light was irradiated, since muc-Si was mixture of a crystal phase and an amorphous phase has the bad mobility when running an amorphous phase compared with the mobility when running the inside of a crystal phase. Furthermore, in the amorphous phase, the so-called photodegradation in which a defect is

generated by irradiation of light and a photoelectrical property deteriorates is produced, and performance traverse of a carrier is worsened. Applying microcrystal silicon to a genuineness semiconductor layer, and improving a short circuit photocurrent and open end voltage, this invention makes photodegradation small and aims substantial [ of a laminated-structure photovoltaic cell ] at raising the improvement in the conversion efficiency of a photovoltaic cell, and productivity.

[0005]

[Means for Solving the Problem] this invention has the semiconductor layer of the pin structure where the laminating of a p type semiconductor layer, a i-type-semiconductor layer, and the n-type-semiconductor layer was carried out, and offers the photovoltaic cell to which the rate of crystallization and hydrogen content of non-single crystal silicon in this i-type-semiconductor layer are characterized by changing in the direction of thickness in the photovoltaic cell which a i-type-semiconductor layer becomes from non-single crystal silicon.

[0006] As non-single-crystal-silicon, microcrystal silicon is desirable in that case. Moreover, it is desirable that the i-type-semiconductor layer contains germanium or C. Specifically,  $\mu\text{c-SiC}$  and  $\mu\text{c-SiGe}$  are used preferably.

[0007] Moreover, this invention has the semiconductor layer of the pin structure where the laminating of a p type semiconductor layer, a i-type-semiconductor layer, and the n-type-semiconductor layer was carried out, and offers the manufacture method of the photovoltaic cell characterized by repeating the change in a material gas flow rate in the case of deposition of the aforementioned non-single-crystal-silicon layer in the manufacture method of a photovoltaic cell that a i-type-semiconductor layer consists of non-single-crystal silicon.

[0008]

[Embodiments of the Invention] In order to form a solar battery without photodegradation, non-single crystal silicon is used for the intrinsic layer of a solar battery in this invention. Microcrystal silicon is used suitable for this invention especially. It exists in the form where the silicon crystal structure and amorphous silicon structure about hundreds of Å or more were joined to microcrystal silicon. The mobility of the carrier in the portion which has the crystal structure is the same level as a single crystal very greatly, and has an absorption coefficient also with usual [ near an amorphous silicon ]. However, the microcrystal silicon which has the absorption coefficient which exceeds an amorphous silicon depending on production conditions can also be proposed, it is thickness far thinner than crystal silicon, and sunlight can be absorbed. Moreover, microcrystal silicon has the far simple manufacture method soon compared with a single crystal amorphously.

[0009] Hereafter, the example of an embodiment concerning this invention is explained.

[0010] (Composition of a photovoltaic cell) Drawing 1 is an example of the cross section of a photovoltaic cell for explaining the concept of this invention in detail. However, this invention is not restricted to the photovoltaic cell of the composition of drawing 1. drawing 1 -- setting -- 108 -- for a transparent conductive layer and 105, as for a i-type-semiconductor layer and 103, a n-type-semiconductor layer and 104 are [ a substrate and 107 / a rear-face electrode and 106 / a p type semiconductor layer and 102 ] transparent electrodes 101 is a current collection electrode which takes out the generated photocurrent. Furthermore, although drawing 1 is composition which carries out incidence of the light to a substrate 108 from a reverse side, by the photovoltaic cell of composition of carrying out incidence of the light, the laminating of each class may be carried out to the turn that drawing 1 is reverse, except for a substrate from a substrate side.

[0011] Hereafter, it explains to the order formed about each class of the photovoltaic cell of this invention in detail.

[0012] (Conductive substrate) The conductive substrate 108 used for this invention consists of metals or these alloys, such as NiCr, stainless steel, and aluminum, Cr, Mo, Au, Nb, Ta, V, Ti, Pt, Pb. Moreover, the thickness of the conductive substrate 108 is usually 10-micrometer or more need from points, such as a mechanical strength on manufacture and handling. As polish processing of a conductive substrate, the front face of a metal substrate is processed in the shape of [ with the acute angle ] zigzag by chemical etching or cutting. The method of processing the front face of a metal substrate by the opportunity-grinding method using particle abrasive materials, such as chemical surface treatment methods, such as chemical polishing and electrolytic polishing, and a diamond, a Carborundum, and an alundum, while controlling irregularity is raised. After grinding a surface of metal, the tip on a multiplex convex is lost by \*\*\*\*\*ing.

[0013] (Rear-face electrode layer) The rear-face electrode 107 used for this invention is an electrode allotted to the rear face of a semiconductor layer to the direction of optical incidence. As a material of a rear-face electrode, alloys, such as metals, such as gold, silver, copper, aluminum, nickel, iron, chromium, molybdenum, a tungsten, titanium, cobalt, a tantalum, niobium, and a zirconium, or stainless steel, are mentioned. Especially a metal with the reflection factor of aluminum, copper, silver, gold, etc. high especially is desirable. When using a metal with a high reflection factor, it can be made to serve as the role of the light reflex layer which reflects again in a semiconductor layer the light which was not able to be absorbed in a semiconductor layer to a rear-face electrode.

[0014] (Transparent conductive layer) The transparent conductive layers 106 are the mainly following purposes, and are arranged between the rear-face electrode layer 107 and a semiconductor layer. First, raise the scattered reflection in the rear face of a photovoltaic cell, and by multiplex interference by the thin film, light is shut up in a photovoltaic cell, and the optical path length in a semiconductor layer is carried in a continuation, and increase the short-circuit current ( $J_{sc}$ ) of a photovoltaic cell. Next, prevent that the metal of the rear-face metallic reflective layer which serves as a rear-face electrode is spread in a semiconductor layer, or starts migration, and a photovoltaic cell carries out a shunt. Moreover, it is preventing the short-circuit generated by defects, such as a pinhole of a semiconductor layer, between the rear-face electrode layers 107 and transparent electrodes 102 which were prepared in the transparent conductive layer on both sides of the semiconductor layer by giving some resistance.

[0015] Moderate resistivity is required as the transparent conductive layer 106 having high permeability in the wavelength field which can absorb a semiconductor layer. Preferably, it is desirable for the permeability of 650nm or more to be 90% or more the optimal 85% or more preferably 80% or more.

[0016] (Semiconductor layer) The thing using IV group alloys, such as a thing using IV group elements, such as Si, C, and germanium, as a material of the semiconductor layer used for this invention or SiGe, SiC, and SiSn, is used.

[0017] moreover, as a semiconductor material used especially suitable for the photoelectromotive-force equipment of this invention in the above semiconductor material a-Si:H (brief sketch of hydrogenation amorphous silicon), a-Si:F, a-Si:H:F, IV groups, such as a-SiGe:H, a-SiGe:F, a-SiGe:H:F, a-SiC:H, a-SiC:F, and a-SiC:H:F, and an IV group alloy system non-single crystal semiconductor material are mentioned.

[0018] Moreover, a semiconductor layer can perform valence-electron control and forbidden-band width-of-face control.

What is necessary is to be independent, or to mix to the aforementioned material gas for deposition film formation, or the aforementioned dilution gas, and just to introduce the raw material compound containing the element used as a valence-electron control agent or a forbidden-band width-of-face control agent in membrane formation space, in case a semiconductor layer is specifically formed.

[0019] Moreover, by valence-electron control, the part is doped by p type and n type, and a semiconductor layer forms the pin junction of a lot at least. And it becomes the so-called composition of a stack cell by carrying out two or more laminatings of the pin junction.

[0020] Moreover, as the formation method of a semiconductor layer, it is formed of various CVD, such as a microwave plasma CVD method, RF plasma CVD method, optical CVD, heat CVD, and the MOCVD method, various vacuum depositions, such as EB vacuum evaporation, MBE, ion plating, and the ion beam method, a sputter, a spray method, print processes, etc. As a method adopted industrially, material gas is decomposed with plasma, and the plasma CVD method made to deposit in the shape of a substrate is found, and is used. Moreover, as a reactor, equipment, continuation membrane formation equipment, etc. of a batch type can use it according to a request.

[0021] In this invention, as a i-type-semiconductor layer, silicon, silicon germanium, a silicon carbide, etc. are made to microcrystal-ize, and are used. Material gas is diluted with a lot of hydrogen as a method for acting as microcrystal Chemicals length, and the method of putting in large power and forming membranes is used in many cases. An example of production equipment is shown in drawing 2. The frequency of 2.45GHz and the microwave of power 20W to 2000W are introduced from the microwave power supply shown in 201. No less than 1.5GHz of frequency of microwave is suitably used from 50MHz besides [ which is industrial frequency ] 2.45GHz. The microwave generated with the microwave power supply of 201 is introduced into the reaction chamber shown in 209 through the waveguide shown in 202. SiH<sub>4</sub> which is material gas is introduced from the line shown in 205. It is introduced from the gas line which shows gas, such as GeH<sub>4</sub>, CH<sub>4</sub>, and H<sub>2</sub>, to 206. Gas is introduced into a reaction chamber 209 from lines 205 and 206. Into a reaction chamber 209, in 200sccm(s) from 5sccm(s), and GeH<sub>4</sub>, 500sccm(s) from 5sccm(s) and CH<sub>4</sub> are introduced by 5sccm(s) to 1000sccm(s), and H<sub>2</sub> is introduced [ SiH<sub>4</sub> / 4 ] by the flow rate, such as 100sccm(s) to 3000sccm(s). By the microwave which carried out incidence from 203, the gas in a reaction chamber 209 will be in the plasma state, and can form the microcrystal-ized film of silicon, SiGe, and SiC on the substrate shown in 204. The gas after decomposition is exhausted by the oil diffusion pump shown in 207, and the pressure in a reaction chamber 209 is maintained at 500mTorr(s) from 10mTorr.

[0022] (Transparent electrode) In this invention, a transparent electrode 102 serves also as a role of an antireflection film by optimizing the thickness while being an electrode by the side of optical incidence which penetrates light. It is required that a transparent electrode 102 has high permeability in the wavelength field which can absorb a semiconductor layer, and that resistivity should be low. Preferably, it is desirable for the permeability in 550nm to be 85% or more more preferably 80% or more. Moreover, it is desirable [ resistivity ] preferably that it is below  $1 \times 10^{-3} \Omega \text{cm}$  below  $5 \times 10^{-3} \Omega \text{cm}$ . As the material, what mixed the conductive oxide of In<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>, ITO (In<sub>2</sub>O<sub>3</sub>+SnO<sub>2</sub>), ZnO and CdO, Cd<sub>2</sub>SnO<sub>4</sub>, TiO<sub>2</sub> and Ta<sub>2</sub>O<sub>5</sub>, Bi<sub>2</sub>O<sub>3</sub>, MoO<sub>3</sub>, and NaXWO<sub>3</sub> grade or these is used suitably. Moreover, you may add the element (dopant) from which conductivity is changed to these compounds.

[0023] the case where a transparent electrode 102 is ZnO as an element (dopant) to which conductivity is changed, for example -- aluminum, In, B, Ga, Si, F, etc. -- moreover -- the case of In<sub>2</sub>O<sub>3</sub> -- Sn, F, Te, Ti, Sb, Pb, etc. -- moreover, in SnO<sub>2</sub>, F, Sb, P, As, In, Tl, Te, W, Cl, Br, I, etc. are used suitably

[0024] Moreover, as the formation method of a transparent electrode 102, a spray method, CVD, a plasma CVD method, an electrocrystallization method, a vacuum deposition method, an ionization vacuum deposition, the sputtering method, the spin turning-on method, the dipping method, etc. are used suitably.

[0025] By using the photovoltaic cell of this invention, an extensive band-gap field which is as amorphous as a \*\* band-gap field like a microcrystal in a band gap is formed, and the band profile which suited the incident-light spectrum can be formed. Moreover, cluster-like hydrogen can be made [ many ] or lessening can obtain easily. For example, by centralizing the hydrogen which became cluster-like near the interface of n/i or p/i, the mechanical stress in an interface is eased and it becomes possible to reduce the defect by interface stress.

[0026] The field with little cluster-like hydrogen can be formed by making for example, membrane formation speed small, and can form a precise non-single crystal semiconductor by such method. Cluster-like hydrogen is formed by carrying out the trap of the hydrogen to the void in a non-single crystal semiconductor etc. A non-single crystal semiconductor with little such cluster-like hydrogen can be formed also by heating and supplying material gas, such as silane gas, and adding oscillating

rotational energy etc. to material gas. Moreover, a non-single crystal semiconductor with little cluster-like hydrogen can be formed by irradiating ion and a hydrogen excitation kind on a front face during thin film formation like hydrogen plasma treatment. Moreover, it is also possible by doping impurities, such as nitrogen, and changing the state of the energy in a network to lessen cluster-like hydrogen. Measurement of the voidage/rate of crystallization of a microcrystal silicon layer is performed by the cross section transverse electromagnetic, the X diffraction, and Raman-scattering measurement. Especially the rate of crystallization of the direction of thickness of a semiconductor film was measured forming membranes in a many wavelength-dispersions type ellipsometry (sow plastic company MOSS-ES4G). many wavelength -- a spectrum -- the ellipsometry was scanned from 250nm of wavelength fields to 850nm using the rotatory polarization child type There was an incident-light angle at 75 degrees. It carries out like this. The spectrum of obtained tanpsi and cosdelta is the formula (D.) of BRUGGEMAN concerning complex-index-of-refraction composition in the amorphous silicon spectrum and crystal silicon spectrum-which were measured beforehand and-existed. [A.G.BRUGGEMAN, ]-[ Ann.Phys. ] (Leipzig) the volume when defining the volume ratio of an amorphous silicon and crystal silicon arbitrarily according to 24,636 (1935), performing spectrum composition, and being best in agreement with a measurement spectrum -- the rate of crystallization was defined with the mixing ratio

[0027] Light is collectable over the latus wavelength field of sunlight by using the photovoltaic cell characterized by having an amorphous layer between a conductivity-type semiconductor layer (a p type semiconductor layer or n-type-semiconductor layer) and the microcrystal silicon layer which has not been doped.

[0028] By using the photovoltaic cell characterized by decreasing gradually, the mobility of the carrier in an interface with the semiconductor layer formed on this SiGe layer can be raised as muc-SiGe is used for a microcrystal silicon layer and the amount of germanium of deposition thickness in this SiGe layer increases.

[0029] By using the photovoltaic cell characterized by increasing gradually, the mobility of the carrier in a bulk field can be raised as muc-SiGe is used for a microcrystal silicon layer and the amount of germanium of deposition thickness in this SiGe layer increases. In addition, the photovoltaic cell of a desired property can be obtained by adjusting the change in the amount of germanium suitably.

[0030] By using for the top layer of a stack type cell the photovoltaic cell characterized by increasing gradually, an optical component with long wavelength is also effectively collectable as muc-SiC is used for a microcrystal silicon layer and the amount of deposition thickness of C in this SiC layer increases.

[0031] Accumulation of a carrier can form a few photovoltaic cell to the membranous depth direction by forming the photovoltaic cell characterized by the amount of dopes of a p type semiconductor layer or a n-type-semiconductor layer changing.

[0032] The interface level of the amorphous phase of a microcrystal phase-boundaries side was sharply reducible by using the photovoltaic cell characterized by repeating the change in a material gas flow rate in the case of deposition of a microcrystal silicon layer.

[0033] a microcrystal silicon layer -- a fluorine -- 0.1atom(s)% to 40atom(s)% -- it can flow without also being able to make into high mobility the substrate side of the optical generation layer which light cannot reach easily, and a carrier accumulating it, if \*\*\*\*\* characterized by adding is used, and an efficient flow can be formed

[0034] By the photovoltaic cell characterized by the stacking tendency of the crystal inside a microcrystal silicon layer changing in the depth direction of a layer, mobility was high and was able to reduce the defect in an p/i interface. Orientation with high (100) mobility is a center, and this makes growth of p layers good by considering as orientation (111) by the p/i interface to crystal grain becoming large according to the interface of a n-type-semiconductor layer.

[0035] In the photovoltaic cell characterized by the stacking tendency of the crystal inside a microcrystal silicon layer changing in the depth direction of a layer, the surrounding amount of hydrogen of crystal grain becomes more than 5atom%, and since termination of the silicon uncombined hand is carried out, the mobility in a grain boundary improves.

[0036] Furthermore, in case a microcrystal layer is formed on n type layer of a cell, the defect of a n-type-semiconductor layer / microcrystal i-type-semiconductor layer interface can be reduced by forming the microcrystal layer of the same phase as n type layer in the direction of an interface.

[0037]

[Example] <Example 1> The example based on this invention which applied 5cmx5cmx0.8mm SUS304 as a base material is shown. SUS304 used for the base material performs pickling with a nitric acid (5vol%) after a heat-and-pressure total, and performs buffing after that. Mirror-plane processing is carried out by buffing and the front face of one side of SUS304 of a base material deposited the aluminum layer with a thickness of 1000A on the mirror-plane side in EB vacuum deposition by resistance heating as a rear-face electrode (metal layer). It carried out to 20A/s in deposition speed.

[0038] The transparent conductive layer on a rear-face electrode was produced by the DC sputtering method which uses a zinc oxide as a target. When carrying out the spatter of the zinc oxide, it carried out by pressure 8mTorr and 2kW of direct current powers using Ar gas. Before deposition of a zinc oxide, as a shutter is closed and a zinc oxide did not accumulate on the substrate front face, it was made to discharge for 15 minutes, and the zinc-oxide target front face was cleaned. Then, the shutter was opened for 30 minutes and the zinc-oxide thin film was formed.

[0039] The n-type-semiconductor layer was formed for the base material by the RF plasma CVD method after zinc-oxide thin film formation. At this time, it was referred to as RF power 200W and pressure 2Torr, and PH3 gas which diluted 200sccm(s) and Si2H6 with 30sccm(s) and H2 for SiH4 to 20 ppm was used 0.5 sccms as material gas.

[0040] Then, the i-type-semiconductor layer was formed. Using RF plasma CVD equipment in formation of a i-type-semiconductor layer, as material gas, flow rate 100sccm was used for SiH<sub>4</sub>, and flow rate 1000sccm and H<sub>2</sub> were used for CH<sub>4</sub> flow rate 2000sccm. Moreover, it could be substrate temperature [ of 300 degrees C ], reaction chamber pressure 400mTorr, and rf power 10kW. During production, it introduced into the reaction chamber by time profile which shows SC-1 of drawing 3, SC-2, SC-3, SC-4, and SC-5 to SiF<sub>4</sub>.

[0041] The rate of crystallization was increasing as the flow rate of SiF<sub>4</sub> increased at this time. For example, when the flow rate of SiH<sub>4</sub> was 0, it was 10%, and at the time of 800sccm, it was 60%.

[0042] The p type semiconductor layer was formed by the RF plasma CVD method after the i-type-semiconductor stratification. At this time, it considered as power 500W and the substrate temperature of 200 degrees C at the power supply using the industrial frequency of 13.56MHz. Moreover, the p type semiconductor layer was formed by pressure 1.5Torr as material gas, using BF<sub>3</sub> who diluted SiH<sub>4</sub> with 20sccm(s) and H<sub>2</sub> to 60 ppm 0.5 sccms.

[0043] Then, the ITO film was formed 650A in thickness with the vacuum deposition of a resistance heating method, and it considered as the transparent electrode. At this time, the inside of a vacuum housing was made into oxygen atmosphere, and was made into pressure 3mTorr and the temperature of 200 degrees C. Furthermore, on the transparent electrode, as a current collection electrode, by EB vacuum deposition, after depositing 300A of Ti, 4000A of Cu(s) was deposited. The solar battery produced as mentioned above is made into - (SC-1) (SC-5).

[0044] The photoelectric conversion efficiency was measured about these solar batteries. Measurement was performed by holding the temperature of a sample at 25 degrees C using the solar simulator which can irradiate the light of a spectrum AM 1.5 and optical on-the-strength 100 mW/cm<sup>2</sup>. Moreover, the open circuit voltage, the short-circuit current, and the curvilinear factor were also measured. A result is shown in Table 1.

[0045]

[Table 1]

表1 SiF<sub>4</sub>による光電変換効率変化

	光電変換効率 [%]	開放電圧 [V]	短絡電流密度 [mA/cm <sup>2</sup> ]	曲線因子
SC-1	7.17	0.45	24.5	0.65
SC-2	7.68	0.48	24.6	0.65
SC-3	7.80	0.48	25.0	0.65
SC-4	6.80	0.45	24.0	0.63
SC-5	6.30	0.90	10.0	0.70

[0046] consequently, SiF<sub>4</sub> amount -- an p/i interface -- low -- carrying out -- an n/i interface -- many -- having carried out (SC-3) -- the property became clear [ a good thing ] most On the contrary, (SC-5) with SiF<sub>4</sub> uniform (SC-4) amount was inferior in the photoelectric conversion efficiency.

[0047] <Example 2> Production conditions other than a microcrystal silicon layer created the sample on the same conditions as an example 1. It was referred to as microwave power 200W, pressure 26mTorr, the substrate temperature of 300 degrees C, and SiH<sub>4</sub> flow-rate 50sccm at the microcrystal silicon layer using the microwave plasma CVD method. Moreover, in that case, GeH<sub>4</sub> was also used as material gas, and the flow rate was changed, as shown in SC-6 of Table 2, and SC-7. Then, the p type semiconductor layer, the transparent electrode, and the current collection electrode were produced on the same conditions as an example 1. Thus, the created data are set to (SC-6) and (SC-7).

[0048] Moreover, the result which measured the rate of crystallization in the microcrystal silicon layer in each conditions is shown in a parenthesis.

[0049]

[Table 2]

表2 GeH<sub>4</sub> 流量

	0~10 分	10~20分	20~30 分
SC-6のGeH <sub>4</sub> 量 [sccm]	20 (10)	30 (20)	40 (30)
SC-7のGeH <sub>4</sub> 量 [sccm]	40 (30)	60 (40)	80 (55)
SC-8のGeH <sub>4</sub> 量 [sccm]	100 (65)	100 (65)	100 (65)

[0050] <Example 1 of comparison> The sample (SC-8) was produced on the same conditions as an example 2 except having fixed GeH<sub>4</sub> flow rate of a microcrystal silicon layer. The conditions at this time are as being shown in SC-8 of Table 2.

[0051] The result which measured the photoelectric conversion efficiency as a result of measuring the mobility of a i-type-semiconductor layer in a time OBUFU light about the sample produced in the example 2 and the example 1 of comparison is shown in Table 3.

[0052]



[Table 3]

表3 移動度と光電変換効率

	移動度 [相対値]	光電変換効率 [%]	開放電圧 (V)	短絡電流密度 (mA/cm <sup>2</sup> )	曲線因子
SC-6	1.1	7.80	0.42	32.0	0.58
SC-7	1.2	9.10	0.38	38.0	0.63
SC-8	1.0	6.98	0.33	42.3	0.50

[0053] As shown in Table 3, by changing GeH<sub>4</sub> amount to GUREDEDDO, mobility is improving and the conversion efficiency is also improving in connection with this. The diameter of crystal grain in an p/i interface is small, and this is considered because the defect in an p/i interface decreased in connection with a bird clapper. Moreover, good short-circuit current density was obtained about all the samples of Table 3. This is considered because the diameter of crystal grain became large by addition of GeH<sub>4</sub>.

[0054] <Example 3> The conditions of crystallization of the microcrystal nature silicon which is genuineness substantially were changed, and the solar battery (SC-9) was produced. First, on the stainless steel substrate, the mixed gas of the rates 1/30 of SiH<sub>4</sub>/H<sub>2</sub> gas ratio was introduced by the plasma CVD method, and the microcrystal silicon film of 100nm of thickness was formed for the substrate temperature of 300 degrees C, and RF power by 200W to 400W. When this microcrystal silicon film was measured by UV reflected light intensity with a wavelength of 280nm, the rate of crystallization was 0.20. The measuring method is as follows.

[0055] If incidence of the ultraviolet rays which came out of the deuterium lamp is carried out to a silicon film with the incident angle of 5 degrees and the reflected light intensity is measured with a spectroscope, the peak of the reflected light will be observed by the wavelength of 280nm by absorption of E2 band (band-gap 4.31eV) peculiar to crystal silicon. Since the height of this peak is, are proportional to the rate of crystallization, i.e., the rate, of the area which a crystal grain child occupies in a silicon film front face, it can ask for the rate of crystallization of the film by comparing with the peak height of the polycrystal silicon film of the rate 1.0 of crystallization measured beforehand.

[0056] The rate of crystallization for which it asked as mentioned above was carrying out simultaneously coincidence at the rate of surface ratio of the crystal grain child who exists in the microcrystal silicon film for which it asked by transmission-electron-microscope observation. Moreover, although the peak intensity of the direction which shows a crystal was obtained according to the X diffraction, when comparing with the polycrystal film, intensity was weak [ the above-mentioned microcrystal semiconductor film ]. furthermore, Raman -- according to the spectrum, the peak was seen near Raman shift 520cm<sup>-1</sup>, and it differed from near [ in the case of being amorphous / 480cm<sup>-1</sup> ]

[0057] Next, the ion implantation equipment was used for the microcrystal silicon film formed on the substrate, silicon ion and the ion from the source of plasma containing a hydrogen ion were accelerated on it, and silicon ion and the hydrogen ion were simultaneously poured into it. The pouring condition introduced 5%SiH<sub>4</sub> of hydrogen dilution gas, and RF power for plasma formation performed [ the acceleration voltage of the ion in 200W and plasma ] 10microA/cm<sup>2</sup> and substrate temperature at the time of pouring for 100kV and ion current density at 350 degrees C. When it pours in for 13 minutes on this condition, the about 5x10<sup>16</sup> total amounts /of ion implantations of silicon ion and a hydrogen ion are [ cm ] 2.

[0058] About the silicon semiconductor film into which the total amount of ion implantations was changed, by changing pouring time shows the result which measured the rate of crystallization to SC-9-1 of Table 4, SC-9-2, and SC-9-3. Measurement of the rate of crystallization was performed like the measurement before an ion implantation.

[0059]

[Table 4]

表4 イオン注入量と結晶化率

	イオン注入量 $\times 10^{18}$ [cm <sup>-2</sup> ]	深さ [Å]	結晶化率 [%]	短絡電流密度 [mA/cm <sup>2</sup> ]
SC-9-1	5	500	50	7.5
		2000	70	
		4000	70	
		6000	70	
		8000	70	
		10000	40	
		12000	20	
		12500	10	
SC-9-2	6	500	60	8
		2000	80	
		4000	80	
		6000	85	
		8000	90	
		10000	80	
		12000	50	
		12500	20	
SC-9-3	7	500	60	7.3
		2000	80	
		4000	80	
		6000	85	
		8000	90	
		10000	70	
		12000	50	
		12500	10	

[0060] Depending on conditions, it is known that crystallization progresses and it is in a microcrystal silicon film if an ion implantation is performed to an amorphous silicon film.

[0061] The result which measured the rate of crystallization about the silicon semiconductor film which carried out the ion implantation like the following, and which produced the amorphous silicon film instead of the microcrystal silicon film, and was produced was 5% or less.

[0062] In addition, SiH<sub>4</sub>/H<sub>2</sub> ratio performed production of an amorphous silicon film by the substrate temperature of 250 degrees C, and RF power 50W using two thirds of gas by the plasma CVD method.

[0063] Compared with the case where an early film is an amorphous silicon film, a desired microcrystal silicon film is obtained with an ion implantation with the little direction in case an early film is a microcrystal silicon film. For example, in order to obtain the microcrystal silicon film of the rate 0.5 of crystallization, in the case of an amorphous silicon film, the total amount of ion implantations is or more [ at least  $3.2 \times 10^{17}$  //cm ] 2 need. Thus, in order to have performed a lot of pourings, when it carries out by ion current density A/cm<sup>2</sup> ( $6.25 \times 10^{13}$  piece/cm<sup>2</sup>, sec) of 10micro which are the usual pouring conditions, it requires almost as long as 85 minutes. On the other hand, in the case of a microcrystal silicon film,  $6 \times 10^{16}$  rates /0.5 of crystallization can be obtained in the amount of ion implantations of 2 cm, and pouring time can be shortened at about 8 minutes and 30 seconds. furthermore -- the system to which power was changed like an example -- pi interface -- the rate of crystallization -- decreasing -- \*\*\*\* -- short-circuit current density -- the rate of crystallization -- most -- decreasing -- carrying out -- \*\*\*\* (SC-9-3) -- it was the best

[0064] <Example 4> In the example 1, only the i-type-semiconductor layer changed the creating method, and created the solar battery (SC-10). The i-type-semiconductor layer was created by the plasma CVD method by forming the microcrystal silicon-carbide film of 100nm of thickness at RF power 400W and the substrate temperature of 250 degrees C. At this time, it considered as production conditions as shown in Table 5, using SiH<sub>4</sub>, SiF<sub>4</sub>, hydrogen, and CH<sub>4</sub> as membrane formation gas.

[0065]

[Table 5]

表 5 成膜ガス

	SiF <sub>4</sub> [sccm]	CH <sub>4</sub> [sccm]	SiH <sub>4</sub> [sccm]	H <sub>2</sub> [sccm]
SC - 10 - 1	0	20	100	100
SC - 10 - 2	20	20	100	100
SC - 10 - 3	40	20	100	100
SC - 10 - 4	60	20	100	100
SC - 10 - 5	80	20	100	100
SC - 10 - 6	100	20	100	100
SC - 10 - 7	120	20	100	100
SC - 10 - 8	140	20	100	100
SC - 10 - 9	160	20	100	100
SC - 10 - 10	180	20	100	100
SC - 10 - 11	200	20	100	100
SC - 10 - 12	100	40	100	100
SC - 10 - 13	100	60	100	100
SC - 10 - 14	100	80	100	100
SC - 10 - 15	100	100	100	100
SC - 10 - 16	100	120	100	100
SC - 10 - 17	100	140	100	100
SC - 10 - 18	100	160	100	100
SC - 10 - 19	100	180	100	100
SC - 10 - 20	100	200	100	100

[0066] The relation between the rate of microcrystal-izing under membrane formation and an assembly time was measured by the many wavelength-dispersions type ellipsometry about the microcrystal thin film formed on conditions as shown in Table 5. A result is shown in drawing 4 .

[0067] The direction in early stages of [ membrane formation ] a microcrystal silicon carbide had the high rate of crystallization, and the rate of crystallization was falling near the p/i interface. When X diffraction measurement investigated the stacking tendency of the sample of an example especially, in (SC-10-1), orientation had become main (100), and orientation was main at (SC-10-2) (110). This showed that orientation was main (100) near the n/i interface. The solar battery of an example 4 had the high conversion efficiency, and when especially used for the top cell of a stack cell, the high conversion efficiency was obtained.

[0068]

[Effect of the Invention] According to this invention, a photoelectric conversion efficiency is high and can obtain the solar battery which was excellent in short-circuit current density and the curvilinear factor.

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CLAIMS

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[Claim(s)]

[Claim 1] The photovoltaic cell to which the rate of crystallization and hydrogen content of non-single crystal silicon in this i-type-semiconductor layer are characterized by changing in the direction of thickness in the photovoltaic cell which it has the semiconductor layer of the pin structure where the laminating of a p type semiconductor layer, a i-type-semiconductor layer, and the n-type-semiconductor layer was carried out, and a i-type-semiconductor layer becomes from non-single crystal silicon.

[Claim 2] The photovoltaic cell according to claim 1 to which the aforementioned i-type-semiconductor layer is characterized by the bird clapper from microcrystal silicon.

[Claim 3] The photovoltaic cell according to claim 1 characterized by the aforementioned i-type-semiconductor layer containing germanium or C.

[Claim 4] The photovoltaic cell according to claim 1 characterized by having an amorphous layer between the type semiconductor layer aforementioned [ p-th ] or a n-type-semiconductor layer, and a i-type-semiconductor layer.

[Claim 5] The photovoltaic cell according to claim 1 characterized by decreasing gradually as the aforementioned i-type-semiconductor layer consists of muc-SiGe and the amount of germanium of deposition thickness in this i-type-semiconductor layer increases.

[Claim 6] The photovoltaic cell according to claim 1 characterized by increasing gradually as the aforementioned microcrystal silicon layer consists of muc-SiGe and the amount of germanium of deposition thickness in this i-type-semiconductor layer increases.

[Claim 7] The photovoltaic cell according to claim 1 characterized by decreasing gradually as the aforementioned microcrystal silicon layer consists of muc-SiC and the amount of germanium of deposition thickness in this i-type-semiconductor layer increases.

[Claim 8] The photovoltaic cell according to claim 1 characterized by the amount of dopes of the type semiconductor layer aforementioned [ p-th ] or the type semiconductor layer aforementioned [ n-th ] changing within a layer.

[Claim 9] the aforementioned i-type-semiconductor layer -- a fluorine -- 0.1atom(s)% to 40atom(s)% -- the photovoltaic cell according to claim 1 characterized by containing

[Claim 10] The photovoltaic cell according to claim 1 characterized by the stacking tendency of the crystal inside the aforementioned i-type-semiconductor layer changing in the depth direction of a layer.

[Claim 11] The photovoltaic cell according to claim 1 characterized by the crystal grain of the aforementioned i-type-semiconductor layer being spherical.

[Claim 12] The manufacture method of the photovoltaic cell characterized by repeating the change in a material gas flow rate in the case of deposition of the aforementioned non-single-crystal-silicon layer in the manufacture method of a photovoltaic cell that have the semiconductor layer of the pin structure where the laminating of a p type semiconductor layer, a i-type-semiconductor layer, and the n-type-semiconductor layer was carried out, and a i-type-semiconductor layer consists of non-single crystal silicon.

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## ABSTRACT:

PROBLEM TO BE SOLVED: To achieve a practically satisfiable film-forming speed and improve a photoelectric conversion characteristic by including a specific amount of phosphorus atom and setting the X-ray or electron ray diffraction intensity of (220) plane to be a specific ratio to the total diffraction intensity.

SOLUTION: This silicon thin film contains 1-100 ppm of phosphorus atom and the diffraction intensity of the (220) plane of the film by X-ray or electron ray diffraction is

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to the formation method of the photovoltaic cell containing a silicon system thin film and it, and a silicon system thin film, and the manufacture method of a photovoltaic cell. The photovoltaic cell of this invention is applied to a solar battery, a sensor, an image sensor, etc.

[0002]

[Description of the Prior Art] Although the method of making it grow up from the liquid phase, such as the cast method, had been performed from the former as the formation method of a silicon system thin film which shows crystallinity, high temperature processing is required and the technical problem towards high mass-production nature and low cost-ization occurred.

[0003] As a means to solve these troubles, as an example about a solar battery "ON THEWAY TOWARDS HIGH EFFICIENCY THIN FILM SILICON SOLAR CELLS BY THE "MICROMORPH" CONCEPT", J.Meier et.al., Mat.Res.Soc.Symp.Proc.Vol.420, and p -- to 3 and 1996 The report of having formed the solar battery of the p-i-n structure of a microcrystal on the 220-degree C substrate of temperature, and having acquired 7.7% of photoelectric conversion efficiency by the low-temperature forming method using the glow discharge by the RF (110MHz) is made. Furthermore, the report of having obtained 13.1% with the solar battery of the laminating mold of amorphous silicon and microcrystal silicon is made by this reference.

[0004]

[Problem(s) to be Solved by the Invention] However, although the microcrystal silicon film by the glow discharge already indicated as mentioned above has the outstanding photoelectric transfer characteristic, there was a trouble that there was nothing on practical use level industrially about membrane formation time amount for it to obtain the needed thickness since membrane formation speed is inadequate.

[0005] Moreover, it is known for the photovoltaic cell using the silicon system thin film in which crystallinity is generally shown that the performance traverse of a carrier is barred by the effect of the incompleteness of the strain produced the dangling bond of the silicon in a grain boundary and near the grain boundary and the crystal itself etc., and the photoelectric transfer characteristic of this photovoltaic cell stops being able to say under it that it is good.

[0006] Although it was possible as a cure for mitigating the effect of the above to raise degree of crystallinity, for that purpose, reduced membrane formation speed, the substrate with electron beam irradiation, laser radiation, a lamp, etc. was heat-treated, and the device of performing film formation for formation of a silicon system thin film and annealing in a hydrogen ambient atmosphere with a repeat was required. These processings had become the factor which lengthens membrane formation time amount and raises cost.

[0007] Then, this invention solves the above-mentioned technical problem, and can manufacture it at the membrane formation speed which is in practical use level industrially, and it aims at offering the silicon system thin film and photovoltaic cell which were excellent in the photoelectric transfer characteristic.

[0008]

[Means for Solving the Problem] This invention contains the Lynn atom 1 ppm or more, and offers a silicon system thin film characterized by a rate of diffraction reinforcement by X-rays or electron diffraction (220) being 30% or more of total diffraction reinforcement.

[0009] Moreover, in a photovoltaic cell which has at least two or more silicon system semiconductor layers which have a mutually different conductivity type on a substrate, at least one of said the silicon system semiconductor layers contains the Lynn atom 1 ppm or more, and this invention offers a photovoltaic cell characterized by having a silicon system thin film whose rate of diffraction reinforcement by X-rays or electron diffraction (220) is 30% or more of total diffraction reinforcement.

[0010] Furthermore, in a method of forming a silicon system thin film on a substrate using a plasma-CVD method, a silicon system thin film formed contains the Lynn atom 1 ppm or more, and this invention offers a formation method of a silicon system thin film characterized by controlling so that a rate of diffraction reinforcement by X-rays or electron diffraction (220) becomes 30% or more of total diffraction reinforcement.

[0011] In addition, this invention is set using a plasma-CVD method to a manufacture method of a photovoltaic cell of having at least a production process which forms on a substrate two or more silicon system semiconductor layers which have a

mutually different conductivity type. At least one of said the silicon system semiconductor layers contains the Lynn atom 1 ppm or more. A manufacture method of a photovoltaic cell characterized by controlling to have a silicon system thin film whose rate of diffraction reinforcement by X-rays or electron diffraction (220) is 30% or more of total diffraction reinforcement is offered.

[0012] As for concentration of the Lynn atom in said silicon system thin film, it is desirable that it is 100 ppm or less. Moreover, as for this silicon system thin film, it is desirable that it is the semiconductor of i mold substantially. Furthermore, as for concentration of the Lynn atom in this silicon system thin film, it is desirable to suppose that it is uneven, and it is desirable to consider as high concentration by substrate side. As for this silicon system thin film, it is desirable to form more preferably 10MHz or more 10GHz or less frequency by plasma-CVD method which used a with a 30MHz or more frequency [ 500MHz or less ] RF. This silicon system thin film may contain germanium or C. As for this RF, it is desirable to impress using an electrode and to set distance between this electrode and said substrate to 3cm or more.

[0013] As for said photovoltaic cell, it is desirable that have at least one pin junction and an i-type semiconductor layer of this pin junction has said silicon system thin film. Moreover, as for this photovoltaic cell, it is desirable that have at least two pin junction and an i-type semiconductor layer of pin junction of a side nearest to a substrate has said silicon system thin film among these pin junction.

[0014]

[Embodiment of the Invention] In order to solve the technical problem mentioned above, as a result of repeating research wholeheartedly, this invention person contains the above-mentioned Lynn atom 1 ppm or more. The silicon system thin film of a configuration of that the rate of the diffraction reinforcement by the X-ray diffraction pattern or the electron ray pattern (220) was formed to total diffraction reinforcement so that it might be 30% or more In spite of promoting inactivation of the grain boundary in a film and could form at a high membrane formation speed, it found out that good crystallinity and the good photoelectric transfer characteristic were shown.

[0015] There are the following operations by making it the above-mentioned configuration.

[0016] Although the silicon in which crystallinity is shown generally had diamond structure and the silicon atom occupies 4 coordination location, in the grain boundary in a crystalline silicon system thin film, especially a microcrystal silicon system thin film, it is thought that there is a portion which the irregular grain boundary which consists of the coordination number different from 4 coordination by distortion of structure, concentration of a rearrangement, etc. produces. If the Lynn atom of ultralow volume is introduced here, it will be thought that the added Lynn atom will have the operation which close inactivates [ operation ] a grain boundary to the aforementioned irregular grain boundary, and makes carrier performance traverse, i.e., mutau product, improve. It becomes possible to form a silicon thin film by high-speed membrane formation, without worsening carrier performance traverse according to this effect.

[0017] As for the concentration of the Lynn atom contained in an above-mentioned silicon system thin film, it is desirable that it is 100 ppm or less. If the concentration of the Lynn atom exceeds 100 ppm, the membranous quality of a silicon system thin film will deteriorate, and there is a possibility that carrier mobility may fall. Especially, when the above-mentioned concentration exceeds 100 ppm in the photovoltaic cell using this silicon system thin film, there is a possibility that photoelectric conversion efficiency may fall.

[0018] Moreover, since the crystalline silicon system thin film in which the field (220) carried out orientation in parallel with a substrate has the channel structure of 6 angle configuration perpendicularly to a substrate side, it is considered to excel in the carrier performance traverse of a direction perpendicular to a substrate side. In addition, with the crystalline silicon of non-orientation, the percentage of the diffraction reinforcement of a field to total (220) of the diffraction reinforcement for the 11 reflection from a low angle side is about 23% so that clearly from an ASTM card. That is, the crystalline silicon system thin film with which the rate of the diffraction reinforcement of a field (220) exceeds 23% will have a stacking tendency in the direction of a field (220). The rate of the diffraction reinforcement of a field is considered especially (220) that the effect of improvement in carrier performance traverse comes to be promoted more in 30% or more of structure. Moreover (220), by having a stacking tendency in a field, distortion of structure and concentration of a rearrangement are controlled and it is thought that formation of a crystalline good thin film is attained.

[0019] Furthermore, the photovoltaic cell of this invention carries out the laminating of two or more silicon system semiconductor layers which show a different conductivity type on a conductive substrate one by one, and is characterized by silicon system semiconductor at least 1 of said two or more silicon system semiconductor layers containing said silicon system thin film. In the photovoltaic cell which carried out the laminating of n mold silicon system semiconductor layer, i mold silicon system semiconductor layer, and the p-type silicon system semiconductor layer one by one especially, it becomes possible to form the photovoltaic cell of the property excellent in said i mold silicon system semiconductor layer which functions as a light absorption layer containing said silicon system thin film. Said i mold silicon semiconductor layer may consist only of said silicon system thin film, and may carry out the laminating of said silicon system thin film and the i-type semiconductor film of another gestalten, such as an amorphous silicon thin film. Moreover, also in the photovoltaic cell which carried out the laminating of n mold silicon system semiconductor layer, i mold silicon system semiconductor layer, and 2 or more sets of p-type silicon system semiconductor layers one by one, it is the same. Moreover, since said silicon system thin film has the features that photodegradation is very small or it does not cause a photodegradation phenomenon, it is using a main light absorption layer as said silicon system thin film, and formation of a photovoltaic cell [ be / or / no photodegradation phenomenon ] with very small photodegradation is attained.

[0020] Moreover, as for the semiconductor layer in the silicon system thin film of this invention, and a photovoltaic cell, it is

desirable to form with the CVD method using the RF whose frequency is 10MHz - 10GHz. Compared with the method of creating from the liquid phase, formation of the silicon system thin film in low temperature is possible for a CVD method, and the formation of said silicon thin film and a photovoltaic cell of it is attained by low cost.

[0021] Moreover, as for the photovoltaic cell of this invention, it is desirable that the concentration of the Lynn atom contained in said silicon system thin film is increasing toward said conductive substrate side. In the field by the side of an early-stages of formation, i.e., said conductivity, substrate, since the diameter of crystal grain is relatively small, said silicon thin film is considered that the density of said irregular grain boundary is also high. Therefore, it is thought effective to introduce more Lynn atoms into the field by the side of said conductive substrate.

[0022] Next, the component of the photovoltaic cell of this invention is explained.

[0023] Drawing 1 is the typical cross section showing an example of the photovoltaic cell of this invention. For 101, as for a semiconductor layer and 103, a conductive substrate and 102 are [ a transparent electrode and 104 ] current collection electrodes among drawing. Moreover, as for a base and 101-2, 101-1 is [ a metal layer and 101-3 ] transperence conductive layers, and these are the configuration members of the conductive substrate 101.

[0024] (Base) As a base 101-1, the plate-like part material and sheet-like member which consist of a metal, resin, glass, ceramics, semiconductor bulk, etc. are used suitably. In the surface, you may have detailed unevenness. It is good also as a configuration in which light carries out incidence from a base side using a transperence base. Moreover, continuation membrane formation using a roll-to-roll process can be performed by making a base into a long configuration. Especially the material that has the flexibility of stainless steel, polyimide, etc. is suitable as a material of a base 101-1.

[0025] (Metal layer) The metal layer 101-2 has a role of an electrode, and a role of a reflecting layer which reflects the light which reached even the base and is made to reuse in a semiconductor layer. As the material, aluminum, Cu, Ag, Au, CuMg, etc. can be used suitably. As the formation method, methods, such as vacuum evaporatono, a spatter, electrocrystallization, and printing, are suitable.

[0026] As for the metal layer 101-2, it is desirable to have unevenness on the surface. The optical path length within the semiconductor layer 102 of the reflected light can be lengthened by that cause, and a short-circuit current can be increased. When a base 101-1 has conductivity, it is not necessary to form a metal layer.

[0027] (Transperence conductive layer) The transperence conductive layer 101-3 increases the scattered reflection of incident light and the reflected light, and has the role which lengthens the optical path length within the semiconductor layer 102. Moreover, it has the role with which the element of the metal layer 101-2 prevents that a lifting photovoltaic cell carries out the shunt of diffusion or the migration to the semiconductor layer 102. Furthermore, it has the role which prevents the short-circuit by the defect of the pinhole of a semiconductor layer etc. by having moderate resistance. As for the conductivity of the transperence conductive layer 101-3, it is desirable that it is below  $10^{-1}$  ( $1/\text{ohm}\cdot\text{cm}$ ) more than  $10^{-8}$  ( $1/\text{ohm}\cdot\text{cm}$ ). Furthermore, as for the transperence conductive layer 101-3, it is desirable to have unevenness on the surface like the metal layer 101-2. As for the transperence conductive layer 101-3, consisting of conductive oxides, such as ZnO and ITO, is desirable, and it is desirable to form using methods, such as vacuum evaporatono, a spatter, CVD, and electrocrystallization. The material for changing conductivity to these conductive oxides may be added.

[0028] (Conductive substrate) By the above method, on a base 101-1, if needed, the laminating of the metal layer 101-2 and the transperence conductive layer 101-3 is carried out, and the conductive substrate 101 is formed. Moreover, in order to make integration of an element easy, an insulating layer may be prepared in the conductive substrate 101 as an interlayer.

[0029] (Semiconductor layer) as the main material of the silicon system thin film of this invention, and the semiconductor layer 102 -- an amorphous phase or a crystal phase -- Si of these mixed phase systems is used further. It may replace with Si and an alloy with Si, C, or germanium may be used. Hydrogen and/or a halogen atom contain in the semiconductor layer 102. The desirable content is 0.1 to 40 atom %. The semiconductor layer 102 may contain oxygen, nitrogen, etc. further. It makes it contain V group element to consider as an III group element and a n-type-semiconductor layer to use a semiconductor layer as a p type semiconductor layer. In the case of a stack cel (photovoltaic cell which has two or more pin junction), the i-type semiconductor layer of the pin junction near an optical incidence side has a large band gap, and it is desirable that a \*\*\*\* band gap becomes narrow to become far pin junction. Moreover, inside i type layer, it is more desirable than the center of the direction of thickness that the minimal value of a band gap is in p type layer approach. a crystalline semiconductor with few dope layers to light absorption by the side of optical incidence (p type layer or n type layer) -- or the large semiconductor of a band gap is suitable.

[0030] (The formation method of a semiconductor layer) In order to form the above-mentioned semiconductor layer 102 and the silicon system thin film of this invention, the RF plasma-CVD method is suitable. Hereafter, the suitable example of the procedure which forms the semiconductor layer 102 by the RF plasma-CVD method is shown.

(1) Decompress the inside of the deposition room (vacuum chamber) which changes into a reduced pressure condition to a predetermined deposition pressure.

(2) Introducing material gas, such as material gas and dilution gas, into the deposition interior of a room, and exhausting the deposition interior of a room with a vacuum pump, set up so that the pressure of the deposition interior of a room may turn into a predetermined deposition pressure.

(3) Set up so that the temperature of a substrate may turn into a predetermined temperature at a heater.

(4) Introduce into said deposition interior of a room the RF oscillated by the RF generator. The introductory method to said deposition interior of a room draws a RF with a waveguide, through dielectric windows, such as alumina ceramics, it introduces into the deposition interior of a room, or it draws a RF with a coaxial cable, and has the method which has



introduced into the deposition interior of a room enough, and is carried out through a metal electrode.

(5) Make the plasma occur in the deposition interior of a room, decompose material gas, and form a deposition film in conductive substrate top 101 arranged in the deposition interior of a room. The semiconductor layer 102 is repeatedly formed for this procedure if needed two or more times.

[0031] As formation conditions for the semiconductor layer 102, 100-450 degrees C and a deposition pressure are raised for the substrate temperature in the deposition interior of a room as conditions with 0.001 - 1 W/cm<sup>3</sup> suitable for 0.5mTorr(s) - 10Torr and RF power.

[0032] The compound which contains the silicon atom of SiH<sub>4</sub>, Si<sub>2</sub>H<sub>6</sub>, and SiF<sub>4</sub> grade as material gas suitable for silicon system thin film formation of the above-mentioned semiconductor layer 102 and this invention and which can be gasified is mentioned. When making it an alloy system, it is desirable to add the compound which contains germanium, C, etc. like GeH<sub>4</sub> or CH<sub>4</sub> further and which can be gasified to material gas. As for material gas, it is desirable to dilute with dilution gas and to introduce into the deposition interior of a room. H<sub>2</sub>, helium, etc. are raised as dilution gas. The compound which furthermore contained nitrogen, oxygen, etc. and which can be gasified may be added as material gas thru/or dilution gas. As dopant gas for using a semiconductor layer as p type layer, B-2 H<sub>6</sub> and BF<sub>3</sub> grade are used. Moreover, PH<sub>3</sub>, PF<sub>3</sub>, etc. are used as dopant gas for using a semiconductor layer as n type layer. As gas for introducing the Lynn atom into the silicon system thin film of this invention, PH<sub>3</sub>, PF<sub>3</sub>, etc. are used suitably.

[0033] It is few, or when [ which are the thin film of a crystal phase, and light absorption, such as SiC, ] depositing the large layer of a band gap, it is desirable the increase of a rate and to carry out and to introduce [ of the dilution gas to material gas ] the RF of comparatively high power.

[0034] (Transparent electrode) Although a transparent electrode 103 has the role of an electrode, it can serve as the role of an antireflection film by setting up the thickness suitably.

[0035] As a material of a transparent electrode 103, ITO, ZnO, and In<sub>2</sub>O<sub>3</sub> grade can be used suitably. As the formation method, methods, such as vacuum evaporation, CVD, a spray, spin-on, and immersion, are suitable. The material from which conductivity is changed to these materials may be added.

[0036] (Current collection electrode) The current collection electrode 104 is formed on a transparent electrode 103, in order to improve current collection effectiveness. The method of forming the metal of an electrode pattern by the spatter, using a mask as the formation method, the method of printing a conductive paste or soldering paste, the method of fixing a metal wire with a conductive paste, etc. are suitable.

[0037] In addition, a protective layer may be formed in both sides of a photovoltaic cell if needed. \*\*\*\*\*, such as a steel plate, may be prepared in the rear face (an optical incidence side and opposite side) of a photovoltaic cell etc. at coincidence.

[0038]

[Example] Although a solar battery is mentioned as an example as a photovoltaic cell and this invention is made concrete in the following examples, these examples do not limit the contents of this invention at all.

[0039] [Example 1] The pin mold photovoltaic cell shown in drawing 3 in the following procedures was formed using the deposition film formation equipment 201 shown in drawing 2.

[0040] Drawing 2 is the typical cross section showing an example of deposition film formation equipment which manufactures the silicon system thin film and photovoltaic cell of this invention. The deposition film formation equipment 201 shown in drawing 2 is constituted when the substrate send container 202, the vacuum housings 211-218 for semiconductor formation, and the substrate rolling-up container 203 join together through the gas gates 221-229. It pierces through each container and each gas gate to this deposition film formation equipment 201, and the band-like conductive substrate 204 is set in it. The band-like conductive substrate 204 begins to be rolled from the bobbin installed in the substrate send container 202, and is rolled round by another bobbin with the substrate rolling-up container 203. The vacuum housings 211-218 for semiconductor formation make glow discharge occur, decompose material gas and make a semiconductor layer to have a discharge room, respectively and deposit on the conductive substrate 204 by it by impressing high-frequency power to the discharge electrodes 241-248 of this discharge interior of a room from RF generators 251-258. Moreover, the gas installation pipes 231-238 for introducing material gas and dilution gas are connected to each vacuum housings 211-218 for semiconductor formation.

[0041] Although the deposition film formation equipment 201 shown in drawing 2 possesses eight vacuum housings for semiconductor formation, in the following examples, by all the vacuum housings for semiconductor formation, it does not need to make glow discharge occur and can choose the existence of the glow discharge in each container in accordance with the lamination of the photovoltaic cell to manufacture. Moreover, the non-illustrated membrane formation field baffle plate for adjusting the touch area of the conductive substrate 204 in each discharge interior of a room and discharge space is formed in each vacuum housing for semiconductor formation, and the thickness of the semiconductor layer formed with each container can be adjusted now by adjusting this.

[0042] Drawing 3 is the typical cross section showing an example of a photovoltaic cell which has the silicon system thin film of this invention. Among drawing, the same sign is given to the same member as drawing 1, and explanation is omitted.

[0043] The semiconductor layer of this photovoltaic cell consists of the amorphous n-type-semiconductor layer 102-1, a microcrystal i-type semiconductor layer 102-2, and a microcrystal p type semiconductor layer 102-3. That is, this photovoltaic cell is the so-called pin mold single cel photovoltaic cell. And the silicon system thin film of this invention is used as a microcrystal i-type semiconductor layer 102-2.

[0044] Hereafter, the manufacture method of the photovoltaic cell of this example is explained using drawing 2 and drawing 3

[0045] First, the band-like base (0.125mm in width of face of 40cm, a length of 200m, thickness) which consists of stainless steel (SUS430BA) was fully degreased and washed, the non-illustrated continuation sputtering system was equipped, and the spatter vacuum evaporation of the aluminum thin film with a thickness of 100nm was carried out using aluminum target. Furthermore, using the ZnO target, the spatter vacuum evaporation of the ZnO thin film with a thickness of 1.2 micrometers was carried out on aluminum thin film, and the band-like conductive substrate 101 (204) was formed.

[0046] Next, it equipped with the bobbin which wound the conductive substrate 204 around the substrate send container 202, and through the gas gate 221 by the side of carrying in of the conductive substrate 204, the vacuum housings 211, 212, 213, 214, 215, 216, 217, and 218 for semiconductor formation, and the gas gate 229 by the side of taking out, tension adjustment was performed so that even the substrate rolling-up container 203 might not have through and the flabby band-like conductive substrate 204. And evacuation was fully carried out to 5x10 to 6 or less Torrs by the evacuation system which consists of a vacuum pump the substrate send container 202, the vacuum housings 211, 212, 213, 214, 215, 216, 217, and 218 for semiconductor formation, and whose substrate rolling-up container 203 are not illustrated.

[0047] Next, the material gas and dilution gas for amorphous n-type-semiconductor stratification are supplied to the vacuum housing 211 for semiconductor formation from the gas installation pipe 231, operating an evacuation system. The material gas and dilution gas for microcrystal i-type semiconductor stratification are introduced into the vacuum housings 212, 213, and 214 for semiconductor formation from the gas installation pipes 232, 233, and 234. The material gas and dilution gas for microcrystal p type semiconductor stratification were supplied to the vacuum housing 215 for semiconductor formation from the gas installation pipe 235. The formation conditions of each class are as being shown in a table 1. Moreover, H<sub>2</sub> gas of 200sccm(s) was supplied to the vacuum housings 216, 217, and 218 for semiconductor formation from the gas installation pipes 236, 237, and 238, and H<sub>2</sub> gas of 500sccm(s) was supplied to each gas gates 221, 222, 223, 224, 225, 226, 227, 228, and 229 as gate gas from each non-illustrated gate gas supply line at coincidence. The exhaust air capacity of an evacuation system was adjusted in this condition, and the pressure in each vacuum housing for semiconductor formation was adjusted to the desired pressure.

[0048] In the place by which the pressure in each vacuum housing for semiconductor formation was stabilized, migration of the band-like conductive substrate 204 was started towards the direction of the substrate send container 202 to the substrate rolling-up container 203. Moving the band-like conductive substrate 204, the non-illustrated infrared lamp heater was turned on and the conductive substrate 204 was heated at 300 degrees C.

[0049] To next, the vacuum housings 211, 212, 213, and 214 for semiconductor formation and the discharge electrodes 241, 242, 243, 244, and 245 in 215 High-frequency power is introduced from RF generators 251, 252, 253, 254, and 255. Glow discharge is occurred in the discharge interior of a room in the vacuum housings 211, 212, 213, and 214 for semiconductor formation, and 215. On the band-like conductive substrate 204, by the vacuum housing 211 for semiconductor formation, the amorphous n-type-semiconductor layer 102-1 (20nm of thickness) By the vacuum housings 212, 213, and 214 for semiconductor formation, the microcrystal i-type semiconductor layer 102-2 (1.5nm of thickness) It was made to carry out sequential formation of the microcrystal p type semiconductor layer 102-3 (10nm of thickness) by the vacuum housing 215 for semiconductor formation, and the pin mold photovoltaic cell shown in [drawing 3](#) was formed (example 1-1). It was here, and the high-frequency power of power 20 nW/cm<sup>3</sup> with a frequency of 100MHz was introduced into the vacuum housings 212, 213, and 214 for semiconductor formation, and the high-frequency power of 13.56 MHz frequency and power 30 mW/cm<sup>3</sup> was introduced into the vacuum housing 215 for semiconductor formation for the high-frequency power of frequency 13.56MHz power 5mW/cm<sup>3</sup> at the vacuum housing 211 for semiconductor formation. In addition, the gap of a discharge electrode and the conductive substrate 204 was fixed to 5cm at this time.

[0050] Next, the RF power introduced into the vacuum housings 212, 213, and 214 for semiconductor formation while adjusting the bearer rate of the membrane formation field baffle plate in each vacuum housing for semiconductor formation and a substrate in the middle of discharge was changed, arranging thickness identically, only the membrane formation speed of the microcrystal i-type semiconductor layer 102-2 differed, and other conditions produced the same photovoltaic cell as the above-mentioned example 1-1 (example 1-1 to 1-5). RF power was taken as 50 mW/cm<sup>3</sup> (example 1-2), 100 mW/cm<sup>3</sup> (example 1-3), 150 mW/cm<sup>3</sup> (example 1-4), and 200 mW/cm<sup>3</sup> (example 1-5) in each example.

[0051] Next, using non-illustrated continuation modularization equipment, the formed band-like photovoltaic cell was carved for every membrane formation speed of a microcrystal i-type semiconductor layer, and each was processed into the solar cell module whose magnitude is 36cmx22cm (example 1-1 to 1-5).

[0052] Moreover, the sample which formed completely the vacuum housing 211 for semiconductor formation and the membrane formation field baffle plate in 215 on closing and a substrate 204 by the i-type semiconductor layer corresponding to an example 1-1 to 1-5 was also produced (example 1-6 to 1-10).

[0053] [Example 1 of a comparison] Except having removed PH<sub>3</sub> (it diluting with H<sub>2</sub> to 5 ppm) from the material gas of a table 1 to the vacuum housings 212, 213, and 214 for semiconductor formation, it is the same method as an example 1, and the solar cell module (example 1-1 to 1-5 of a comparison) and the sample (example 1-6 to 1-10 of a comparison) were created.

[0054] Next, the photoelectric conversion efficiency of the solar cell module created in the example 1 and the example 1 of a comparison was measured using the solar simulator (AM1.5, 100 mW/cm<sup>2</sup>). Moreover, diffraction reinforcement of the created sample was measured using X-ray diffraction equipment, and quantitative analysis of the concentration of the Lynn atom to Si atom of the sample created by SIMS was carried out.

[0055] The photoelectric conversion efficiency of the diffraction reinforcement to the membrane formation speed of an i-type semiconductor layer of an example 1 and the example 1 of a comparison, the concentration of the Lynn atom to Si atom in an i-type semiconductor layer, and the total diffraction reinforcement (220) in the X-ray diffraction peak of an i-type semiconductor layer which is a solar cell module comparatively is shown in a table 2.

[0056] As shown in a table 2, even if the solar cell module of the example 1-1 to 1-5 containing the microcrystal i-type semiconductor layer containing 1 ppm or more of Lynn atoms raises membrane formation speed as compared with the solar cell module of the example 1-1 to 1-5 of a comparison containing the microcrystal i-type semiconductor layer which does not contain only less than 1 ppm of Lynn atoms, it does not almost have decline in photoelectric conversion efficiency. Even if it manufactures the silicon system thin film and photovoltaic cell of this invention using high-speed membrane formation from the above thing, it turns out that photoelectrical change effectiveness has the outstanding feature of hardly falling.

[0057] [Example 2] On condition that the example 1-4, changing the gap of the vacuum housings 212 and 213 for semiconductor formation, and the discharge electrodes 242, 243, and 244 in 214 and the conductive substrate 204 to 3-10cm, the photovoltaic cell of a configuration of being shown in drawing 3 was created, and the solar cell module (example 2-1 to 2-3) was created like the example 1. The sample (example 2-4 to 2-6) furthermore formed by the i-type semiconductor layer was created.

[0058] [Example 2 of a comparison] On the same conditions as an example 2, the photovoltaic cell of a configuration of setting the gap of the semiconductor vacuum devices 212 and 213, and the discharge electrodes 242, 243, and 244 in 214 and the conductive substrate 204 to 2cm, and being shown in drawing 3 was created, and the solar cell module (example 2-1 of a comparison) was created like the example 2. The sample (example 2-2 of a comparison) furthermore formed by the i-type semiconductor layer was created.

[0059] Next, the measurement same about the solar cell module and sample which were created in the example 2 and the example 2 of a comparison as an example 1 and the example 1 of a comparison was performed. A result is shown in a table 3.

[0060] As shown in a table 3, the solar cell module of the example 2-1 to 2-3 whose percentage of the diffraction reinforcement to the total diffraction reinforcement (220) in an X-ray diffraction peak is 30% or more is excellent in photoelectric conversion efficiency as compared with the solar cell module of the example 2-1 of a comparison this whose percentage is less than 30%. Moreover, in order to make this rate into 30% or more, it turns out that it is suitable to set the gap of a discharge electrode and a conductive substrate to 3cm or more. As mentioned above, it turns out that the silicon system thin film and photovoltaic cell of this invention have the outstanding feature that photoelectric conversion efficiency is excellent.

[0061] [Example 3] The tandem-die photovoltaic cell of the pin/pin mold of the configuration of drawing 4 was formed using the deposition film formation equipment 201 shown in drawing 2.

[0062] Drawing 4 is the typical cross section showing an example of a photovoltaic cell which has the silicon system thin film of this invention. Among drawing, the same sign is given to the same member as drawing 1 and drawing 3, and explanation is omitted.

[0063] On the pin junction shown in drawing 3, this photovoltaic cell carries out the laminating of the pin junction which consists of the amorphous n-type-semiconductor layer 102-4, an amorphous i-type semiconductor layer 102-5, and a microcrystal p type semiconductor layer 102-6 further, and forms the semiconductor layer.

[0064] The bottom cel (pin configuration by the side of a substrate) of the photovoltaic cell of this tandem die It creates on condition that an example 1-4. A top cel (pin junction by the side of optical incidence) By the vacuum housing 216 for semiconductor formation, the amorphous n-type-semiconductor layer 102-4 The amorphous i-type semiconductor layer 102-5 was created by the vacuum housing 217 for semiconductor formation, the microcrystal p type semiconductor layer 102-6 was created by the vacuum housing 218 for semiconductor formation, and it considered as the pin junction which an i-type semiconductor layer becomes from an amorphous layer.

[0065] The formation conditions of the amorphous n-type-semiconductor layer 102-4 and the microcrystal p type semiconductor layer 102-6 presupposed that it is the same as that of the formation conditions of the n-type-semiconductor layer shown in a table 1, respectively, and the formation conditions of a p type semiconductor layer among top cels. Moreover, the formation conditions of the amorphous i-type semiconductor layer 102-5 set SiH<sub>4</sub>:50sccm, H<sub>2</sub>:500sccm, and substrate temperature 220 degrees C, and set the pressure to 1.2Torr(s) for material gas.

[0066] Hereafter, the solar cell module (example 3) was created like the example 1.

[0067] [Example 3 of a comparison] The photovoltaic cell of the tandem die of the pin/pin mold of a configuration of being shown in drawing 5 was formed like the example 3. The photovoltaic cell of a tandem die shown in drawing 5 is the same as the photovoltaic cell shown in drawing 4 except the point which is using the i-type semiconductor layer of a bottom cel as the amorphous i-type semiconductor layer 102-7. In this example of a comparison, it created on the same conditions as an example 3 except creation of this layer 102-7. And the solar cell module (example 3-1 of a comparison) was created like the example 3. The creation conditions of the i-type semiconductor layer 102-7 presupposed that it is the same as that of the amorphous i-type semiconductor layer 102-5. Moreover, the sample (example 3-2 of a comparison) in which only 102 to i-type semiconductor layer 7 portion of a bottom cel was formed was created.

[0068] The diffraction peak was not accepted although diffraction reinforcement of the sample (example 3-2 of a comparison) created using X-ray diffraction equipment was measured.

[0069] Next, the photoelectric conversion efficiency of the created solar cell module was measured using the solar simulator (AM1.5, 100 mW/cm<sup>2</sup>). Then, where this solar cell module is held at 50 degrees C, the false sunlight of AM1.5 and 100

mW/cm<sup>2</sup> was irradiated for 500 hours, and the rate of photodegradation of the photoelectric conversion efficiency of the solar cell module by optical irradiation time was investigated. The result is shown in a table 4.

[0070] As shown in a table 4, as compared with the solar cell module of the example 3-1 of a comparison, as for the solar cell module of the example 3 containing the silicon thin film of this invention, the rate of photodegradation is improved sharply. The above thing shows having the outstanding feature that the photovoltaic cell of this invention has a small rate of photodegradation.

[0071] [Example 4] Except having made into twice the example 1-4 the amount of PH<sub>3</sub> (it dilutes with H<sub>2</sub> to 5 ppm) supplied to the vacuum housing 212 for semiconductor formation, it is the same conditions as an example 1-4, and the solar cell module (example 4) was created.

[0072] The photoelectric conversion efficiency of the created solar cell module was measured using the solar simulator (AM1.5, 100 mW/cm<sup>2</sup>). The solar cell module of an example 4 showed one 1.1 times the photoelectric conversion efficiency of this compared with the solar cell module of an example 1-4, it is increasing the concentration of the Lynn atom by the conductive substrate side, and the effect of this invention became still larger.

[0073]

[A table 1]

表 1

n 型 半 導 体 層	原料ガス	SiH <sub>4</sub> : 20sccm H <sub>2</sub> : 100sccm PH <sub>3</sub> (H <sub>2</sub> で2%に希釈) : 30sccm
	基板温度	300℃
	圧 力	1.0Torr
i 型 半 導 体 層	原料ガス	SiH <sub>4</sub> : 30sccm H <sub>2</sub> : 1.0slm PH <sub>3</sub> (H <sub>2</sub> で5ppmに希釈) : 2.0sccm
	基板温度	300℃
	圧 力	300mTorr
p 型 半 導 体 層	原料ガス	SiH <sub>4</sub> : 10sccm H <sub>2</sub> : 800sccm BH <sub>3</sub> (H <sub>2</sub> で2%に希釈) : 100sccm
	基板温度	200℃
	圧 力	1.2Torr

[0074]

[A table 2]

表 2

	成膜速度 (nm/s)	リン原子濃度 (ppm)	(220) の割合 (%)	光電変換効率 *
実施例1-1、1-6	0.01	3ppm	60	1
実施例1-2、1-7	0.1	3ppm	60	0.98
実施例1-3、1-8	0.5	3ppm	58	0.98
実施例1-4、1-9	1.0	3ppm	55	0.97
実施例1-5、1-10	2.0	3ppm	55	0.95
比較例1-1、1-6	0.01	< 1ppm	60	1
比較例1-2、1-7	0.1	< 1ppm	60	0.95
比較例1-3、1-8	0.5	< 1ppm	55	0.87
比較例1-4、1-9	1.0	< 1ppm	50	0.82
比較例1-5、1-10	2.0	< 1ppm	50	0.70

\*光電変換効率は、それぞれの実施例は実施例1-1を1に規格化した値であり、それぞれの比較例は比較例1-1の値を1に規格化した値である。

[0075]

[A table 3]

表 3

	基板-電極距離 (cm)	(220) の割合 (%)	リン原子濃度 (ppm)	光電変換効率 *
実施例 2-1、2-4	3	45	3	1
実施例 2-2、2-5	5	55	3	1.02
実施例 2-3、2-6	10	55	3	1.01
比較例 2-1、2-2	2	25	3	0.85

\* 光電変換効率は、実施例 2-1 の値を 1 に規格化した値である。

[0076]

[A table 4]

表 4

	擬似太陽光 500 時間照射後の光劣化率 *
実施例 3	1
比較例 3-2	2.5

\* 擬似太陽光 500 時間照射後の光劣化率は実施例 3 の値を 1 に規格化した値

[0077]

[Effect of the Invention] As mentioned above, the grain boundary in a silicon thin film is inactivated by forming a silicon system thin film so that the Lynn atom 1 ppm or more may be contained and the rate of the diffraction reinforcement by X-rays or electron diffraction (220) may become 30% or more of total diffraction reinforcement. Furthermore, the photovoltaic cell which has the photoelectric conversion efficiency excellent in forming the photovoltaic cell which carried out the laminating of two or more silicon system semiconductor layers which have different polarity on a conductive substrate one by one as said silicon system thin film contained in silicon system semiconductor at least 1 of said two or more silicon system semiconductor layers (especially i-type semiconductor layer) is obtained.

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[Translation done.]

\* NOTICES \*

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

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CLAIMS

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[Claim(s)]

[Claim 1] A silicon system thin film which contains the Lynn atom 1 ppm or more, and is characterized by a rate of diffraction reinforcement by X-rays or electron diffraction (220) being 30% or more of total diffraction reinforcement.

[Claim 2] A silicon system thin film according to claim 1 characterized by containing the Lynn atom 100 ppm or less.

[Claim 3] A silicon system thin film according to claim 1 characterized by being the semiconductor of i mold substantially.

[Claim 4] A silicon system thin film according to claim 1 characterized by concentration of the Lynn atom contained in said silicon system thin film being uneven.

[Claim 5] A silicon system thin film according to claim 1 characterized by being formed by plasma-CVD method using a with a 10MHz or more frequency [ 10GHz or less ] RF.

[Claim 6] A silicon system thin film according to claim 5 characterized by being formed by plasma-CVD method using a with a 30MHz or more frequency [ 500MHz or less ] RF.

[Claim 7] A silicon system thin film according to claim 1 characterized by containing germanium or C.

[Claim 8] A photovoltaic cell characterized by for at least one of said the silicon system semiconductor layers containing the Lynn atom 1 ppm or more, and having a silicon system thin film whose rate of diffraction reinforcement by X-rays or electron diffraction (220) is 30% or more of total diffraction reinforcement in a photovoltaic cell which has at least two or more silicon system semiconductor layers which have a mutually different conductivity type on a substrate.

[Claim 9] A photovoltaic cell according to claim 8 characterized by said silicon system thin film containing the Lynn atom 100 ppm or less.

[Claim 10] A photovoltaic cell according to claim 8 characterized by said silicon system thin film being the semiconductor of i mold substantially.

[Claim 11] A photovoltaic cell according to claim 8 characterized by having at least one pin junction and an i-type semiconductor layer of this pin junction having said silicon system thin film.

[Claim 12] A photovoltaic cell according to claim 8 characterized by concentration of the Lynn atom contained in said silicon system thin film being high at said substrate side.

[Claim 13] A photovoltaic cell according to claim 8 characterized by said substrate being a conductive substrate.

[Claim 14] A photovoltaic cell according to claim 8 characterized by forming said silicon system thin film by plasma-CVD method using a with a 10MHz or more frequency [ 10GHz or less ] RF.

[Claim 15] A photovoltaic cell according to claim 14 characterized by forming said silicon system thin film by plasma-CVD method using a with a 30MHz or more frequency [ 500MHz or less ] RF.

[Claim 16] A photovoltaic cell according to claim 8 characterized by said silicon system thin film containing germanium or C.

[Claim 17] A photovoltaic cell according to claim 8 characterized by having at least two pin junction and an i-type semiconductor layer of pin junction of a side nearest to a substrate having said silicon system thin film among these pin junction.

[Claim 18] A formation method of a silicon system thin film characterized by controlling so that a silicon system thin film formed contains the Lynn atom 1 ppm or more in a method of forming a silicon system thin film on a substrate using a plasma-CVD method and a rate of diffraction reinforcement by X-rays or electron diffraction (220) becomes 30% or more of total diffraction reinforcement.

[Claim 19] A formation method of a silicon system thin film according to claim 18 characterized by controlling so that a silicon system thin film formed contains the Lynn atom 100 ppm or less.

[Claim 20] A formation method of a silicon system thin film according to claim 18 characterized by controlling so that a silicon system thin film formed serves as an i-type semiconductor.

[Claim 21] A formation method of a silicon system thin film according to claim 18 characterized by controlling so that concentration of the Lynn atom contained in a silicon system thin film formed becomes high by said substrate side.

[Claim 22] A formation method of a silicon system thin film according to claim 18 characterized by using a with a 10MHz or more frequency [ 10GHz or less ] RF.

[Claim 23] A formation method of a silicon system thin film according to claim 22 characterized by using a with a 30MHz or more frequency [ 500MHz or less ] RF.

[Claim 24] A formation method of a silicon system thin film according to claim 22 characterized by impressing said RF using

an electrode and setting distance between this electrode and said substrate to 3cm or more.

[Claim 25] In a manufacture method of a photovoltaic cell of having at least a production process which forms on a substrate two or more silicon system semiconductor layers which have a mutually different conductivity type using a plasma-CVD method A manufacture method of a photovoltaic cell characterized by controlling for at least one of said the silicon system semiconductor layers to contain the Lynn atom 1 ppm or more, and to have a silicon system thin film whose rate of diffraction reinforcement by X-rays or electron diffraction (220) is 30% or more of total diffraction reinforcement.

[Claim 26] A manufacture method of a photovoltaic cell according to claim 25 characterized by controlling so that said silicon system thin film contains the Lynn atom 100 ppm or less.

[Claim 27] A manufacture method of a photovoltaic cell according to claim 25 or 26 characterized by controlling so that said silicon system thin film serves as an i-type semiconductor.

[Claim 28] A manufacture method of a photovoltaic cell according to claim 25 characterized by controlling so that concentration of the Lynn atom contained in said silicon system thin film becomes high by said substrate side.

[Claim 29] A manufacture method of a photovoltaic cell according to claim 25 characterized by forming said silicon system thin film using a with a 10MHz or more frequency [ 10GHz or less ] RF.

[Claim 30] A manufacture method of a photovoltaic cell according to claim 29 characterized by forming said silicon system thin film using a with a 30MHz or more frequency [ 500MHz or less ] RF.

[Claim 31] A manufacture method of a photovoltaic cell according to claim 29 characterized by impressing said RF using an electrode and setting distance between this electrode and said substrate to 3cm or more.

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[Translation done.]